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DIFFUSION IN THE THERMAL DEGRADATION OF NC BASE PROPELLANTS

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A somewhat general discussion of diffusion in nitrocellulous base propellants is followed by a discussion of a kinetic model which predicts in a qualitative manner the features of the growth and decay of the various derivatives of 2NDPA during thermal degradation.

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CONTENTS

INTRODUCTION

It has been known for many years that nitrocellulose (NC) and nitroglycerin (NG) are not stable and decompose. However, very little is known about the decomposition process. It was found empirically that the addition of certain compounds apparently slowed the decomposition process or at least hindered a catastrophic explosion. This hindering of the explosive process occurs by the removal of NO_2 by chemical reaction with the additional compounds or stabilizers as they are called. It seems apparent that diffusion must occur in these materials for the stabilizer to be able to do its work. yet little or nothing is known about diffusion in NC or NC/NG base propellants. A general discussion of diffusion is followed by a discussion of an explicit model for stabilizer reaction with NO_2 via diffusion of the latter.

DIFFUSION

There are several types of experimental evidence which indicate that some sort of diffusion takes place during thermal decomposition of propellant. Gas is given off during thermal decomposition. Several different gases have been detected in this process. This indicated a general breakup of nitrocellulose and nitroglycerin (ref 1). However, it is not clear whether these gases come from surface layers or from the bulk, thus indicating bulk diffusion. Perhaps more direct evidence for bulk diffusion comes from the conversion of the stabilizer into its nitroderivatives by the addition of nitro groups (ref 2). It appears as if this process can only take place by NO_x groups (where x is 1, 2 or 3) breaking off from NC (and/or NG) and diffusing until captured by the stabilizer or its derivatives. Alternately, it is necessary to assume that the much larger stabilizer molecules are mobile and diffuse. The latter seems unlikely.

Evidence has been presented for NG diffusion under some conditions. NG has been observed to collect on the surface during heat treatment, thus indicating NG diffusion from the bulk to the surface (ref 3). The exact conditions under which NG diffusion takes place have not been determined.

The activation energies for diffusion of any type in NC base propellants have not been determined or identified as such. Overall or global activation energies have been determined, but the parts of these energies which could be due to diffusion have not been separated out. In fact, throughout the literature, the activation energies which have been measured have been associated with bond breaking only and not with diffusion. In simple ionic crystals, such as alkali halides and silver halides, very clever techniques have been used to separate the activation energies for diffusion from the energies for bond breaking. Unfortunately the techniques used in the simple ionic crystalline solids can not be used in propellant polymer solids.

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In general, the global activation energies which have been observed during propellant thermal decomposition have been found to increase with increasing temperature of observation, thus indicating the possibility of different processes in different temperature ranges (refs 1 and 4). It is also necessary to consider the possibility that the simple gas molecules which are detected on thermal decomposition, e.g., NO, N_2O, CO_2, NO_2, CO and N_2 move easily through the propellant matrix at least in some directions. There will be a specific activation energy for diffusion for each type of gas molecule and also most probably an activation energy for bond breaking for each molecular species. Clearly more work must be done to establish the role of diffusion in the thermal decomposition of NC base propellant materials.

Diffusion in polymer systems (such as NC) is more complex than in many other types of solid materials. For example, the diffusion coefficient may not be a constant at any given temperature but may depend on quantities such as the concentration (ref 5). In addition, the diffusion coefficient may be different along the direction of the polymer chain than perpendicular to it. The diffusion of many simple gases has been measured in a variety of polymers. The diffusion coefficients have been found to vary over several orders of magnitude for the same simple gas molecules in different polymers (ref 6). Thus, it is very difficult or impossible to estimate the magnitude of the diffusion coefficients of the same simple gases in NC systems although these same simple gases are evolved during thermal decomposition.

An effort was made to estimate the maximum number of thermally activated jumps an NO_x unit must make after bond scission to arrive at a stabilizer molecule for a double base rocket propellant. Many simplifying assumptions were made including uniform distribution of the various ingredients in the propellant and also that an NG molecule occupies the same space as one NC ring. The separation of the stabilizer molecules in NC ring lengths was then estimated. The maximum distance which an NO_x unit must make is then one half of the separation distance between stabilizer molecules. The number of jumps, n, in a random walk process is given by

$$n = \frac{R^2}{r^2}$$

where R is the net displacement in n jumps and r is the length of one jump (ref 7). Using this formula, the maximum number of jumps in terms of NC ring lengths which an NO_x species must make after scission from NC to arrive at a stabilizer molecule was found to be about 10. If the elementary jump distance is smaller than one NC ring length the number of jumps will be larger.

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KINETIC MODEL

As an example of diffusion in a propellant, consider the thermal degradation of a double base rocket propellant containing two nitro diphenylamine (2NDPA) as the stabilizer. It is assumed that the NO_x species produced by thermal degradation of NC and NG diffuse randomly until captured by the stabilizer or its derivatives. The latter are 2NDPA + b(NO_x) where b is a small integer indicating the number of NO_x captured previously by the stabilizer molecule. While it is not known whether it is NO, NO_2, or NO_3, which diffuses, the net result of capture at the stabilizer (or its derivatives) is the addition of a NO_2 group to the stabilizer or its derivatives.

For the purpose of generating a kinetic model to describe the capture of NO_x by the stabilizer or its derivatives, the following are defined:

Let w = concentration of 2NDPA

Let y = concentration of
2,4 Dinitro DPA
2,4' Dinitro DPA

Let z = concentration of
2,4,4' Trinitro DPA
2.2',4 Trinitro DPA

Let r = concentration of 2,2', 4,4' Tetranitro DPA

Let s = concentration of end product (simplifying assumption to demonstrate model)

where all compounds in the right column (except 2NDPA) are derivatives of 2NDPA. For simplicity it is assumed that 2,4 Dinitro DPA and 2,4' Dinitro DPA and the two trinitro DPAs, respectively, have the same cross sections for capture and so are not separated. That this is approximately the case can be seen by an inspection of figure 1. The following reactions are assumed to occur as 2NDPA and its derivatives capture NO_x groups

$$w + NO_x \xrightarrow{\;k_1'\;} y$$

$$y + NO_x \xrightarrow{\;k_2'\;} z$$

$$z + NO_x \xrightarrow{\;k_3'\;} r$$

$$r + NO_x \xrightarrow{\;k_4'\;} s \tag{1}$$

where k_1, k_2, k_3, and k_4 are rate constants as used in equations 2 through 6. The differential equations which describe the reactions can be written as

$$\frac{dw}{dt} = k_1'(NO_x)w = k_1 w \tag{2}$$

$$\frac{dy}{dt} = k_1'(NO_x)w - k_2'(NO_x)y = k_1 w - k_2 y \tag{3}$$

$$\frac{dz}{dt} = k_2'(NO_x)y - k_3'(NO_x)z = k_2 y - k_3 z \tag{4}$$

$$\frac{dr}{dt} = k_3'(NO_x)z - k_4'(NO_x)r = k_3 z - k_4 r \tag{5}$$

$$\frac{ds}{dt} = k_4'(NO_x)r = k_4 r \tag{6}$$

where the concentration of diffusing (NO_x) is assumed to be independent of time to obtain the right side of equations 2 through 6. The boundary conditions are

at $t = o$

$$w = w_o \tag{7}$$

$$y = z = r = s = o$$

The solutions to equations 2 thorugh 6 with the boundary conditions are as follows

$$w = w_o\, e^{-k_1 t} \tag{8}$$

$$y = \frac{k_1\, w_o}{(k_2 - k_1)} \left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{9}$$

$$z = \frac{k_1\, k_2\, w_o}{(k_2 - k_1)} \left[\frac{\left(e^{-k_1 t} - e^{-k_3 t}\right)}{(k_3 - k_1)} - \frac{\left(e^{-k_2 t} - e^{-k_3 t}\right)}{(k_3 - k_2)} \right] \tag{10}$$

$$r = \frac{k_1\, k_2\, k_3\, w_o}{(k_2 - k_1)} \left[\frac{\left(e^{-k_1 t} - e^{-k_4 t}\right)}{(k_4 - k_1)\,(k_3 - k_1)} - \frac{\left(e^{-k_2 t} - e^{-k_4 t}\right)}{(k_4 - k_2)\,(k_3 - k_2)} + \right. $$
$$\left. \frac{\left(e^{-k_3 t} - e^{-k_4 t}\right)\,(k_2 - k_1)}{(k_4 - k_3)\,(k_3 - k_2)\,(k_3 - k_1)} \right] \tag{11}$$

$$S = \frac{k_1\, k_2\, k_3\, k_4\, w_o}{(k_1 - k_2)} \left[\frac{1}{(k_1 - k_4)\,(k_1 - k_3)} \left(\frac{\left(1 - e^{-k_4 t}\right)}{k_4} - \frac{\left(1 - e^{-k_1 t}\right)}{k_1} \right) + \right. $$
$$\frac{1}{(k_2 - k_4)\,(k_2 - k_3)} \left(\frac{\left(1 - e^{-k_2 t}\right)}{k_2} - \frac{\left(1 - e^{-k_4 t}\right)}{k_4} \right) + $$
$$\left. \frac{(k_1 - k_2)}{(k_3 - k_4)\,(k_2 - k_3)\,(k_1 - k_3)} \left(\frac{\left(1 - e^{-k_4 t}\right)}{k_4} - \frac{\left(1 - e^{-k_3 t}\right)}{k_3} \right) \right] \tag{12}$$

In addition to satisfying the boundary conditions these solutions have the following properties

1. at t=0 w and y have finite slopes (13)

2. at t = o z, r and s have zero slopes (14)

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3. y, z and r have maxima as a function of time (15)

4. as $t \to \infty$, $s \to w_0$ and $w, y, z, r \to 0$ (16)

5. for all times $w + y + z + r + s = w_0$ (17)

The quantities w, y, z, r and s from equations 8 through 12 are plotted in figure 2 versus time for a particular set of rate constants. These are

$k_1 = 1.0$

$k_2 = 0.5$

$k_3 = 0.25$

$k_4 = 0.125$

These values of the rate constants were chosen to show that the kinetic model predictions can be similar to available experimental results. The curves of figure 1 are actual measured concentrations of 2NDPA and its derivatives as determined by thin layer chromotography as a function of time at $90°$ C for a double base rocket propellant (ref 8). The curves of figure 2 reproduce qualitatively many of the features of figure 1, such as equations 13 through 17, thus justifying assumptions made in setting up the kinetic model. In addition, the decay of the concentration of 2NDPA in a double base rocket propellant has been found recently to be exponential with a finite initial slope as predicted by equation 8, the initial slopes for the dinitro DPAs have finite values as predicted by equation 9, the initial slope for tinitro DPA is zero as predicted by equation 10, and the concentration of dinitro DPA has a maximum as a function of time as predicted by equation 9.[1,2] The isomers for the model were choosen on the bases of those reported at that time (ref 8). More recently, other isomers have been reported, mostly at other temperatures.[1,2] It is straight forward to include all isomers in the model in such a way as to separate the concentrations of the various isomers.

As noted above it is assumed in writing the right side of the differential equations 2 through 6 that the concentration of diffusing (NO_x) is independent of time for the times of interest. Thus, the rate of production of NO_x must equal the rate of capture of NO_x.

1. G. K. Landram and R. J. Bazuk, Private Communications
2. D. Robertson, Private Communication

This is at best only an approximation and may account for some of the differences between figures 1 and 2. The model does, however, indicate how diffusion can play a role in the thermal degradation of propellant.

DISCUSSION

In summary, it can be said that although there is ample evidence for diffusion in the thermal degradation of NC and NC/NG propellants, there is little in the way of experiments to understand this diffusion. This thermal degradation may be rate limited by diffusion, i.e., the time for NO_x to diffuse from the site of production to the site of capture, it may be rate limited by bond breaking to produce NO_x, it may be rate limited by the rate of reaction of NO_x with the stabilizer molecule after arrival of NO_x at the stabilizer site, or it may be limited by some combination of these processes. It may be possible to distinguish between some of these possibilities by kinetic studies of thermal degradation of NC and NG with and without stabilizer. Global activation energies may be gotten from the temperature dependence of the rate constants of the kinetic model fit to experimental data. However, additional work will be necessary to understand the meaning of these energies. The kinetic model does give a qualitative description of the conversion of stabilizer into its derivatives and the model can be easily extended to include all of the derivatives, as noted above. It should be possible by a comparison of the model with experiment to determine the conditions for the release of red fumes. Thus, the model could then be used to predict the lifetimes of propellant in other cases.
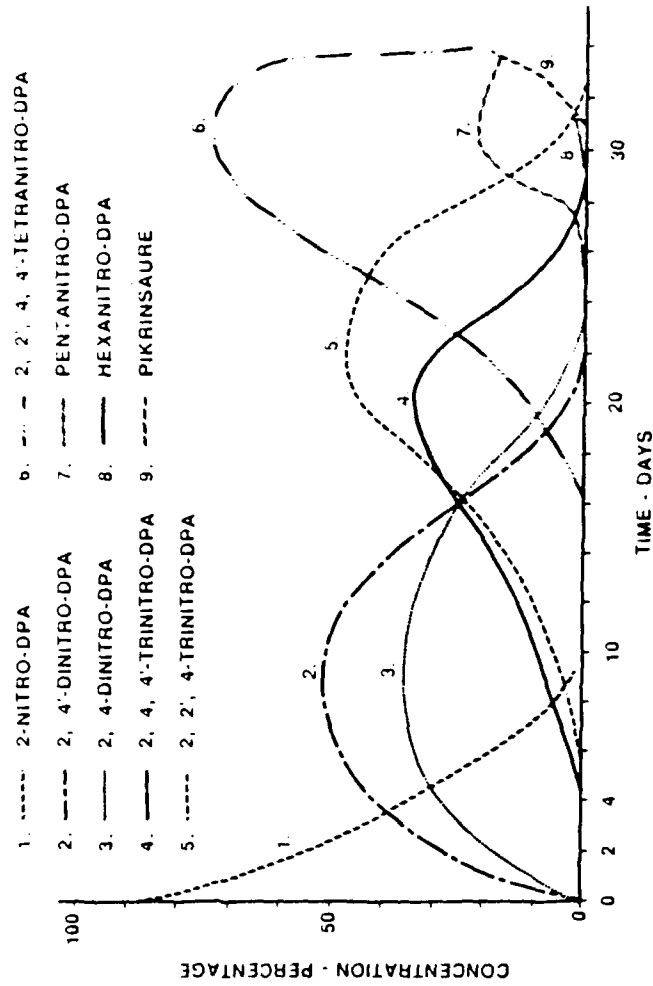
Figure 1. Measured concentrations of 2NDPA and its nitro derivatives as a function of time in days at 90° C. Measurements by thin layer chromatography (ref 2).

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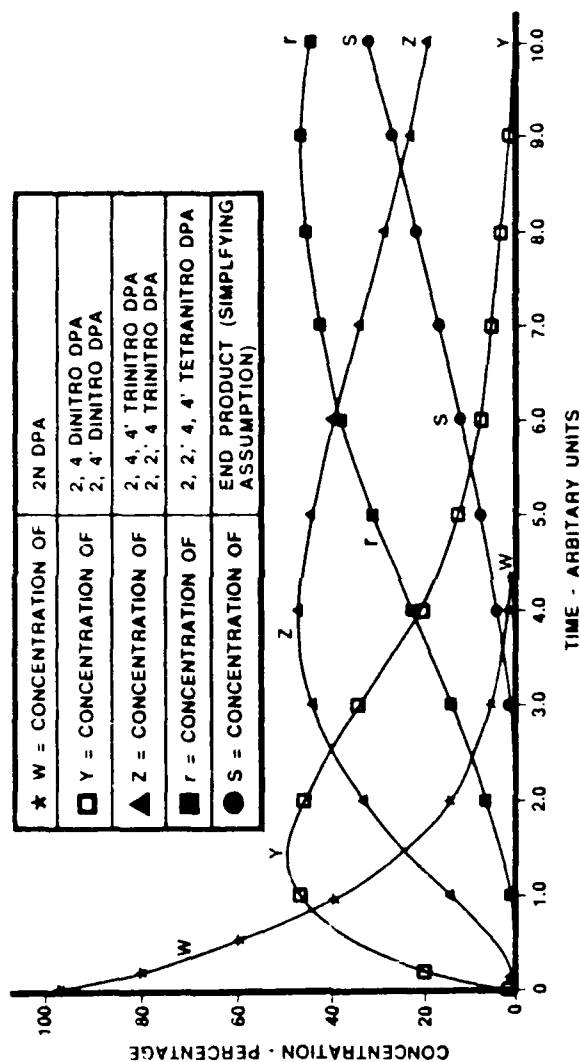# CALCULATIONS FROM KINETIC MODEL

Figure 2. Calculated concentrations of 2NDPA and its nitro derivatives as a function of time

REFERENCES

1. Leider, H.R., and Seaton, D.L., "Gas Evolution and Weight Loss From Thermal Decomposition of PBX-9404 Below 100°C", UCRL 52692, 1979.

2. Hartratt, R., The Evaluation of the Stability of Propellants by Means of Quantitative Determination of the Stabilizer Derivatives, Proc. of International Symposium on Gun Propellants, Picatinny Arsenal, 1973 (see also ref 3).

3. Schroeder, W.A., et. al., "Degradation Products in Decomposition of Double Base Propellants", Ind. Engr. Chem, 41 2819, 1949.

4. See for example, Leider, H.R., "Degradation of the Molecular Weight of Cellulose Nitrate on Thermal Aging", LLNL UCRL 53163, 1981.

5. Diffusion in Polymers, Crank, J., and Park, G.S., Eds., Academic Press, London and New York, pg. 2, 1969.

6. Ibid, pg. 46.

7. Shewmon, P., Diffusion in Solids, McGraw-Hill Book Company, New York, pg. 49, 1963.

8. Robertson, D., Richter, T.A., and Slagg, N., "M55 Assessment Program", Technical Report ARAED-TR-88005, 1988.

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